SUPPORTING INFORMATION

Two-photon spectroscopy of tungsten(0) arylisocyanides using nanosecond-pulsed excitation

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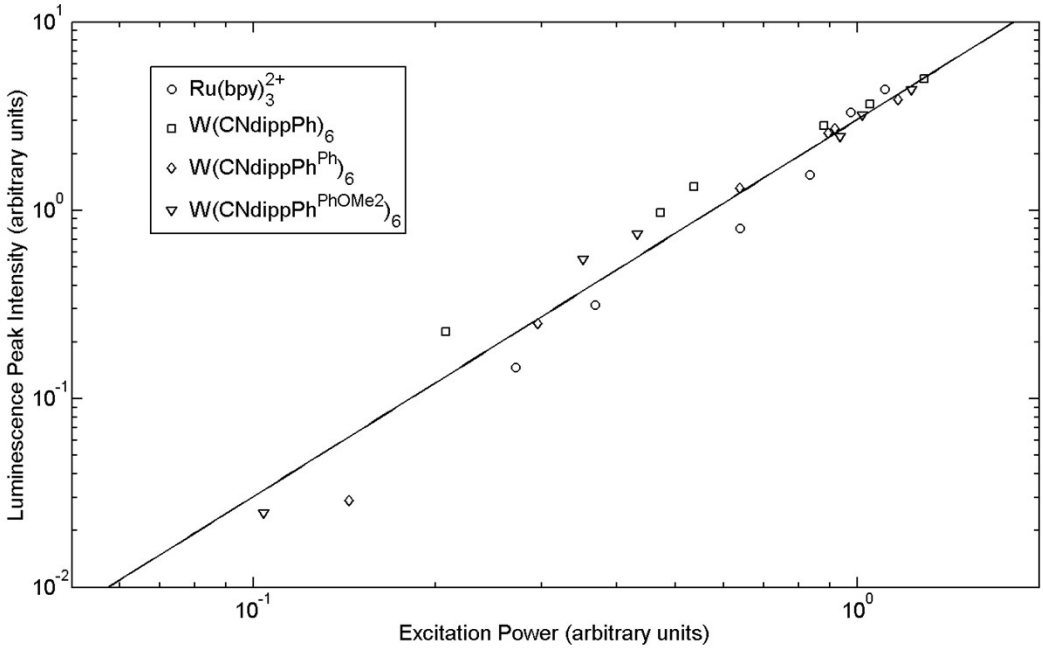

Figure S1. Dependence of the emission intensity of $[Ru(bpy)_3]^{2+}$ and $W(CNAr)_6$ complexes on laser power at λ = 847.6 nm, displayed on a logarithmic scale. Each data set was fit to a linear function, with slopes varying from m = 1.7-2.3. The solid line shown corresponds to a slope of 2, indicating a quadratic power-dependence. Deviation from slope = 2 mainly originated from difficulties measuring low excitation powers.

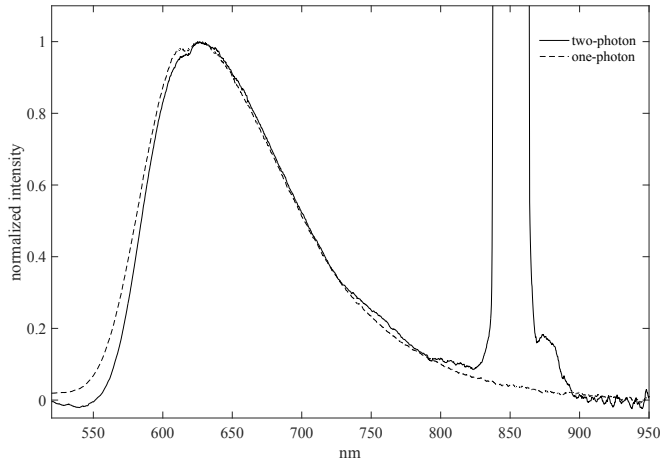

Figure S2. Normalized one- and two-photon luminescence spectra of $[Ru(bpy)_3]^{2+}$ in deionized water. The solid line corresponds to two-photon excitation at λ = 847.6 nm (as indicated by the scattered peak at 850 nm), while the dashed line corresponds to one-photon excitation at λ = 500 nm. There were no significant differences in the two spectra.

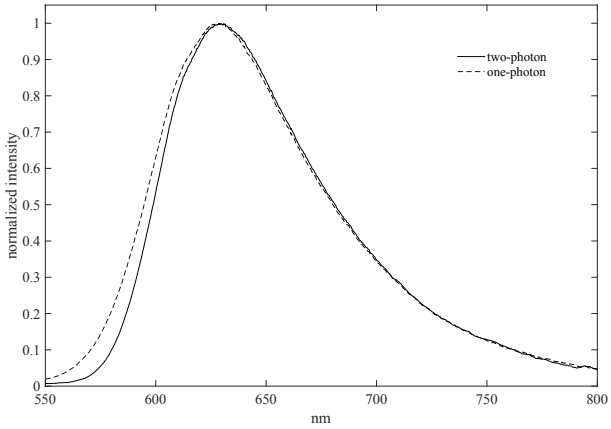

Figure S3. Normalized emission spectra of $W(CNdippPh^{OMe2})_6$ in THF obtained via one- and two-photon excitation. The solid line corresponds to two-photon excitation at λ = 847.6, while the dashed line corresponds to one-photon excitation at λ = 490 nm. There were no significant differences in the two spectra, and it was assumed that changing the solvent from THF to MTHF would have minor effects on the one- versus two-photon chemistry

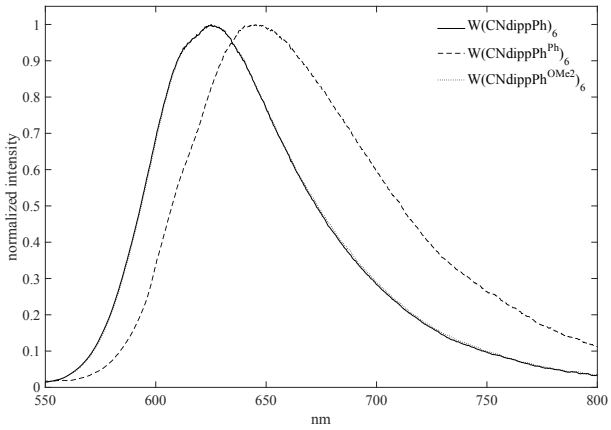

Figure S4. Normalized emission spectra of $W(CNAr)_6$ complexes in MTHF obtained by two-photon excitation at λ = 847.6 nm. The emission spectra of $W(CNdippPh)_6$ and $W(CNdippPh^{OMe2})_6$, solid and dotted lines respectively, are indistinguishable and blue-shifted from the $W(CNdippPh^{Ph})_6$ emission spectrum, the dashed line.

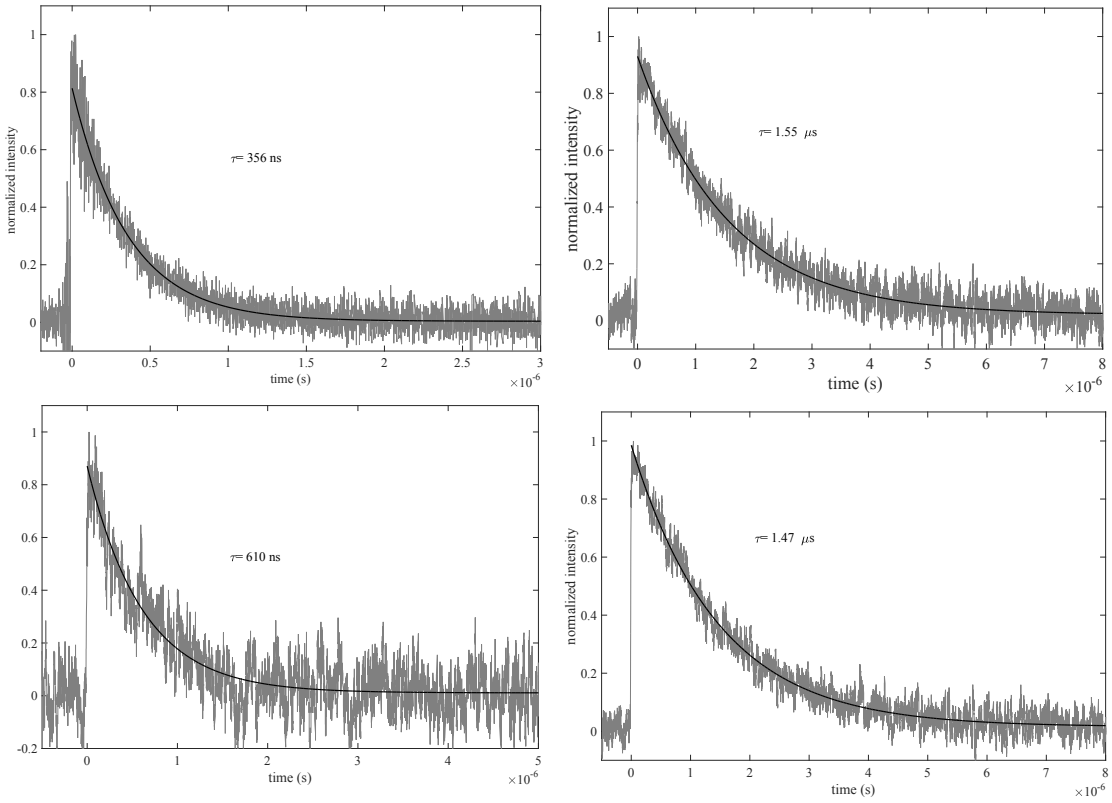

Figure S5. Time-resolved decays of $[Ru(bpy)_3]^{2+}$ (top left), $W(CNdippPh)_6$ (top right) $W(CNdippPh^{Ph})_6$ (bottom left), and $W(CNdippPh^{OMe2})_6$ (bottom right) upon two-photon excitation at λ = 847.6 nm. The data were all fit to monoexponential decays (solid lines), with lifetimes: τ = 356 ns, 1.55 μs, 610 ns, and 1.47 μs, respectively. The short lifetime of $[Ru(bpy)_3]^{2+}$ indicates that the sample was not well-degassed, however, it matches the reported two- and one-photon excitation lifetimes reported by Castellano et al. for aerated $[Ru(bpy)_3]^{2+}$, τ = 363 ± 4 ns and 360± 4 ns, respectively.[1] The lifetimes of the $W(CNAr)_6$ complexes in MTHF are similar to the one-photon lifetimes observed by Sattler et al. of the samples in THF, with differences arising from the solvent.[2]

Absolute Cross Section Determinations

Absolute TPA cross sections were measured relative to fluorescein in H_2O (pH 11) as a standard.[3, 4] Laser excitation wavelength was 811 nm; the beam was collimated to a diameter of ~2 mm. Sample luminescence was collected with a 1-mm diameter optical fiber and directed to an Ocean Optics USB-4000 spectrometer. Luminescence was integrated for 50 s, and 4 accumulations were averaged. Each sample was measure three times. Luminescence spectra were corrected for dark signal and spectral response of the optical system. Results are listed in Table S1. The TPA spectra in Figure 4 of the main text were produced by scaling the relative TPA spectra to the absolute cross section at 811 nm.

Table S1. Measurement parameters for TPA cross section determinations.

Dye	C_{dye}, μM	<F> (σ)[a]	Φ	n	δ_{dye}/δ_{fl} [b]	δ_{811nm}, GM
Fluorescein, H_2O pH 11	77.8[c]	36 (12)	0.97[d]	1.334	1	21[e]
$W(CNdippPh)_6$	15.6[f]	180 (58)	0.25[g]	1.406	94	1966
$W(CNdippPh^{Ph})_6$	5.7[f]	29 (6)	0.12[g]	1.406	83	1740
$W(CNdippPh^{OMe2})_6$	25.1[f]	150 (16)	0.26[g]	1.406	47	978

[a] Fluorescence intensity integrated across the full band profile; standard deviation of multiple measurements in parentheses.

[b] Cross section of sample dye relative to fluorescein: $\frac{\delta_{dye}}{\delta_{fl}} = \frac{\langle F_{dye} \rangle}{\Phi_{dye} C_{dye} n_{dye}} \frac{\Phi_{fl} C_{fl} n_{fl}}{\langle F_{fl} \rangle}$

[c] Determined using the 322-nm extinction coefficient reported in reference 3.

[d] From reference 5.

[e] From references 3, 4.

[f] Determined using the extinction coefficients reported in reference 2.

[g] Adjusted from values in tetrahydrofuran (reference 2) according to Eq. 2 in the main text.

References

1. F. N. Castellano, H. Malak, I. Gryczynski and J. R. Lakowicz, *Inorganic Chemistry*, 1997, **36**, 5548-5551.
2. W. Sattler, L. M. Henling, J. R. Winkler and H. B. Gray, *Journal of the American Chemical Society*, 2015, **137**, 1198-1205.
3. S. de Reguardati, J. Pahapill, A. Mikhailov, Y. Stepanenko and A. Rebane, *Opt. Express*, 2016, **24**, 9053-9066.
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